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the heat exchange surface of the film reactor. This film is contacted with gaseous sulfur trioxide to produce a substantially complete reaction between the reactants to form a reaction mixture that is thereafter converted into a desirable detergent product.

The alpha-olefins that are used are derived from any convenient process, for example, wax cracking, ethylene buildup and by dehydrating the primary alcohols obtained by hydrogenating fatty acids or their esters, e.g. those obtained from palm oil, tallow, coconut oil and olive oil. Vinylidene branching occasionally occurs as a by-product in some preparative methods. The present invention can tolerate amounts of vinylidene branched olefins and internal olefins in the starting material up to levels of 15% by weight, or even more. Although these by-products do not interfere with the sulfonation reaction, it is nevertheless a preferred embodiment of the present invention to run the sulfonation reaction with alpha-olefins wherein the vinylidene branched in internal compounds are held to a minimum, i.e. below 10% by weight.

Alpha-olefins which can be used in the present invention include 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene and 1-eicosene. Mixtures of these compounds can also be used.

The sulfur trioxide sulfonating agent used in the present invention is used as a gas reactant. It is used with a diluent such as any of the commonly used inert materials, e.g. nitrogen, air, etc. The volumetric ratio of diluent to sulfur trioxide should be in the range of from 10:1 to 100:1, and preferably within a range of 15:1 to 75:1.

Preferably the sulfur trioxide sulfonating agent of this invention is uncomplexed. A complexed sulfur trioxide reactant can be used in the present invention, but is normally avoided due to the need to later remove the complexing agent. Failure to remove the complexing agents commonly used can result in a detergent composition that does not perform properly. If the particular complexing agent being employed with the sulfur trioxide does not hamper the present process, affect the detergency performance of the end product or can be removed, such complexed sulfur trioxides can be used.

The proportions of the sulfur trioxide sulfonating agent to the alpha-olefin raw material employed in carrying out the sulfonation reaction can vary within relatively wide limits ranging from less than stoichiometric amounts to stoichiometric amounts, to an excess of the sulfonating agent. It is preferred, however, to run a sulfonation reaction in which at least a stoichiometric amount of sulfonating agent is used. The molar amount of sulfonating agent can range from 0% to 25% and, preferably from 10% to 20% of the sulfonating agent, over the alpha-olefin. That is, the molar ratio of varorous sulfur trioxide to alpha-olefin should be from 1.0:1 to 1.25:1. The preferred molar ratio is from 1.1:1 to 1.2:1.

In addition to the respective amounts of sulfur trioxide and olefin hydrocarbon employed, the rate of mixing the gaseous uncomplexed sulfur trioxide sulfonating agent and the liquid alpha-olefin is also important. For the thin film sulfonation process of this invention, a range for the addition should be between 0.3 to 0.7 pound of sulfur trioxide per pound of liquid olefin per minute. If less than the prescribed rates are used, the reaction will require an inordinately long time resulting in a deterioration in the color of the sulfonated acid mix and higher levels of unreacted starting olefin. If the prescribed rates are exceeded, the composition of the desired olefin sulfonation reaction product will be altered and the color will be adversely affected due to the tendency of having localized high concentrations of sulfur trioxide.

The temperature at which the sulfonation reaction takes place depends largely on the nature of the reactants and the different processing systems which can be employed. Under ordinary conditions, however, the sulfonating temperatures can range from 32° F. to 180° F. but should

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preferably be within the range of 45° F. to 100° F. At temperatures below 32° F., problems can arise involving the solidification of the starting alpha-olefin raw materials together with other problems which may require special apparatus. Allowing the temperature to exceed 180° F. causes a discoloration and generally inferior reaction product.

The length of time for conducting the sulfonation reaction varies over a relatively short time range. In order to achieve the desired balance of components in the end product reaction mix the time of reaction in the sulfonation reaction must be from 12 seconds to 50 seconds, preferably from 15 seconds to 30 seconds. Reaction times in excess of 50 seconds will cause the formation of excess disulfonates and alkene-sulfonates which in turn adversely affects the performance characteristics of the detergent composition. A reaction time of less than 12 seconds is undesirable because of the resultant high percentage of unreacted olefins in the sulfonation reaction mix and consequent poor detergent composition produced therefrom. As a result of conducting the sulfonation reaction at the above specified times and other stated conditions and thereafter processing the sulfonated reaction mix as hereinafter discussed there is obtained a composition containing a blend of components eminently satisfactory as a detergent composition.

The pressure used in the sulfonation reaction can vary over a wide range. Preferably 8 p.s.i.g. to 20 p.s.i.g. pressure is employed in the top of the film reactor. The pressure at the bottom or outlet end of the thin film reactor will be less than the above noted pressure—the amount being dependent on the length of the reactor, temperature, and reactant flow rates. Most preferably the pressure at the top of the reactor is maintained between 8 p.s.i.g. and 14 p.s.i.g.

The acid reactant mix obtained at the bottom of the thin film reactor at the above process conditions is immediately dropped into another reactor container where it comes into contact with a lower alcohol, i.e. an alcohol having from 1 to 4 carbon atoms. Examples of such alcohols are methanol, ethanol, n-propanol, isopropanol, n-butanol and isobutanol. The time between the sulfonation step and contact with the alcohol is quite critical to obtaining the end product desired by the process of this invention. That is, if more than 5 seconds elapse between sulfonation and alcohol contact, the end product composition will consist of an excess of disulfonate and alkene sulfonate. Another drawback encountered when the elapsed time between sulfonation and alcohol contact is greater than about 5 seconds is the fact that an undesired dark-colored product will be obtained. Preferably as little time as possible elapses between the end of the sulfonation reaction and initial contact with the lower alcohol. This is accomplished most efficiently by allowing the sulfonation reaction mix to drop directly into a reactor mix containing the lower alcohol.

The lower alcohol and sulfonated acid mix is allowed to react for from 5 min. to 60 min. at 32° F. to 150° F. Preferably the reaction is carried out for 15 min. to 30 min. at 70° F. to 105° F. On a molar basis, the alcohol to sulfonated reaction mix is from 1.5:1 to 20:1. Preferably 8 to 10 moles of lower alcohol is present for each mole of sulfonated reaction mix.

The above reaction mix is next neutralized by the addition of an aqueous alkali solution. The temperature of the alkali solution mix is not critical since the neutralization reaction will occur readily over a broad temperature range. The aqueous alkali solution consists of any strongly basic compound such as sodium, potassium and ammonium hydroxide, the corresponding oxides, carbonates, mono-, di-, tri- and tetraethanolamine or substituted ammonium hydroxides. Other alkali solutions will be apparent to those skilled in the art. The amount of alkali employed in this step ranges from 1 to 1.2 moles alkali per mole of reaction mix.